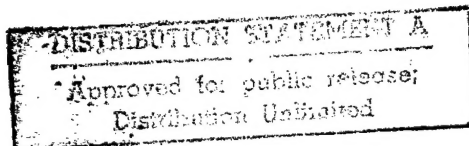


OTS: 60-11,628

JPRS: 2652

10 August 1960



THE EFFECT OF MOLECULAR STRUCTURE ON THE VELOCITY OF  
THE IONIC AND ATOMIC REACTIONS OF ISOTOPE EXCHANGE

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by M. B. Neyman, Yu. M. Shapovalov,  
and V. B. Miller

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JPRS: 2652  
CSO: 3543-N

THE EFFECT OF MOLECULAR STRUCTURE ON THE VELOCITY  
OF THE IONIC AND ATOMIC REACTIONS OF ISOTOPE EX-  
CHANGE. I. THE EFFECT OF LENGTHENING THE CARBON  
CHAIN OF THE ALKYL RADICAL ON THE RATE OF ISOTOPE  
EXCHANGE OF AN ALKYL HALIDE WITH HALIDE IONS

[This is a translation of an article by M. B. Neyman, Yu. M. Shapovalov, and V. B. Miller in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXVIII, No 7, Moscow, 1954, pages 1243-1256.]

At the present time the importance of the problem concerning the connection between molecules' structures and their reaction capacity is universally accepted. It should be pointed out that the theoretical foundations of this trend were laid more than 90 years ago by A. M. Butlerov, who developed the structural theory of chemical compounds. A. M. Butlerov on many occasions wrote about the necessity of paying attention to the mutual effects of separate atoms on each other [2].

The Butlerov ideas regarding the structural effect on the reaction ability were developed by V. V. Markovnikov [3]. Generalizations advanced by V. V. Markovnikov, among them his rule concerning addition of hydrogen halides to olefins, are widely used in chemical investigations. Following this trend, one of the founders of the chemical kinetics, N. A. Menshutkin, carried out classical work of studying the effect of the alkyl iodine radical RJ structure on the velocity of its reaction with triethanamine [4].

For the last thirty years, a great number of works concerning the study of halide activities, other atoms, and the atom groups and their dependents from the structure of radicals connected with them were carried out, for instance by B. V. Tronov [5, 6], P. Petrenko-Krichenko [7, 8], and by many authors abroad [9, 10].

Unfortunately, the mentioned investigations do not offer a complete quantitative characterization of the kinetic

properties of the studied reactions and this hinders and in some cases makes impossible generalization and theoretical treatment of the obtained results. Therefore, it would be of great scientific interest to study systematically the reaction capabilities of atoms entering into a combination of compounds of different structure, for instance some simple reaction with a known mechanism. Approaching this study, we selected as an object the study of a reaction of an isotope exchange of alkylhalides with ions and atoms of halides.

Up to the present time there are approximately 50 published works dealing with halide isotope exchange [11]. It should be noted, however, that the great majority of the published works dealing with isotope exchange are of a quantitative character. Investigators often selected studies of casual objects and treated the obtained results from the standpoint of the defective "theory of resonance" and other idealistic conceptions.

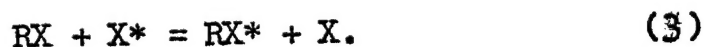
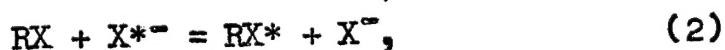
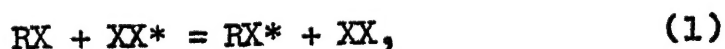
Taking into account the great importance of the problem of the dependence of reaction capability on the structure, and further to develop theories advanced by A. M. Butlerov, we established as the purpose of our present work collection of supplemental material related to the effect of the structure of halide derivatives of the aliphatic series on the velocity constant and the active energy of their isotope exchange. Considering this problem we were determined, while adhering strictly to the Butlerov structure theory, nevertheless to bring into the problem of the mutual effect of atoms certain new essential elements in connection with the present-day state of the development of chemical science.

In the times of A. M. Butlerov, there was insufficient experimental basis for differentiation of the various types of chemical reaction. Therefore A. M. Butlerov and also V. V. Markovnikov did not find it necessary to consider the question of the possibility of discussion of various effects of changing structure on the reaction capability in the case of reactions of various types.

Things are different today. As a result of vigorous development of chemical kinetics in the twentieth century, and especially after the great October Socialist Revolution, we recognize today the following types of homogeneous chemical reactions: molecular reactions (molecules with molecules), ionic (ions with molecules and ions), and radical-chain (proceeding with participation of atoms and radicals.)

Contemporary theoretical conceptions and the experimental data indicate that in the great majority of cases the molecular reactions proceed with a slower speed than the reactions of ions and atoms. These conceptions of types of reactions were developed with particular clarity in works of N. N. Semenov [12-14].

On the basis of contemporary ideas about the mechanism of the chemical process, we set for ourselves a problem of relative study of the isotope exchange velocity of one and the same halidealkyl with molecules, ions and atoms according to reactions:



In our experiments we arranged to carry out the molecular exchange in cyclohexane solutions in darkness, the atom exchange also in cyclohexanol solutions, generating the atom photochemically, and the ion exchange in alcohol solutions of an alkyl halide and dissociating on ions of a halide salt.

In conformity with the conclusions of the theory, the molecular exchange reaction (1), as was demonstrated in our experiments, proceeds at a slower rate than the ion or atom exchange reactions (2) and (3).

Proceeding from the above-indicated deliberations, we were determined not only to study the effect of the structure on the velocity of the isotope exchange but also to conduct a comparative study of the effect of a series of structures of bromine- and iodine-derivatives on the velocity of their isotope exchange with ions and atoms of the corresponding halides.

In the present article, we present the results of our experiments in connection with the study of the mechanism and the velocity of the isotope exchange  $RX + X^{*-} = RX^* + X^-$ , where X-bromine and iodine, and R-radical of normal structure  $CH_3$ ,  $C_2H_5$ , or  $C_3H_7$ .

### EXPERIMENTAL METHOD

For our experiments we used chemically-pure compounds  $\text{CH}_3\text{Br}$ ,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ , and  $\text{C}_3\text{H}_7\text{I}$  which were purified from the admixture of free halides by repeated washing with an aqueous solution of sulfite. The possible traces of sulfite solution were removed by triple shaking with distilled water. After that alkyl halides were dried with potassium chloride and carefully distilled. For these experiments medium fractions, usually boiling within the limits of  $0.3\text{-}0.5^\circ$ , were used.

The boiling temperatures and the refractive indexes of the substances used in the experiments are shown in Table 1.

Table 1  
Constants of the Used Substances

Substance	T - Boiling Temp. $^\circ\text{C}$		$n_D^{20}$	
	Our determination	Published data	Our determination	Published data
$\text{CH}_3\text{Br}$ .....	4.0	4.6	-	-
$\text{C}_2\text{H}_5\text{Br}$ .....	38.3	38.0	1.424	1.424
$\text{C}_3\text{H}_7\text{Br}$ .....	70.8	70.9	1.434	1.434
$\text{CH}_3\text{I}$ .....	42.5	42.6	1.530	1.530
$\text{C}_2\text{H}_5\text{I}$ .....	72.0	72.2	-	-
$\text{C}_3\text{H}_7\text{I}$ .....	102.0	102.4	1.504	1.505

As is apparent from the table, the constants determined by us practically coincide with the published data [15] and this testifies to the purity of compounds used in our work.

Solutions of alkyl halides and the sodium salts of halides were prepared in ethyl alcohol, containing 10 percent water. Experiments related to the study of kinetics exchange were conducted in an installation shown in Fig 1. The reaction container I was welded inside the flask 2, through which there circulated water from the ultrathermostat. The tempera-

ture, measured by means of thermostat 3, was kept constant with variations  $\pm 0.1^\circ \text{C}$ . To the sodium halide solution, placed in container 1, through the funnel 4, a measured quantity of halide alcohol solution was introduced. The time of mixing was noted and the experiment of the kinetics study commenced. The concentration of the resulting substances usually was equal to 0.1 mole/l. From time to time samples were sucked out from the reaction container into the buret 11, and for this purpose it was necessary to close stopcocks 10, 12, and 13, and open stopcocks 8 and 9. Always the same quantity of liquid was removed.

In the case when liquid passed the mark in the buret the cock 12 was opened and the excess of solution was transferred back into the reaction container. The removed sample was removed into the trap 14 or into the separating funnel depending on the accepted methods of the compound separation.

In the case of reaction  $\text{CH}_3\text{Br} + \text{NaBr}^*$  methyl bromide was distilled in a vacuum at depressed temperature and after than bromine which was in form of  $\text{NaBr}^*$  was precipitated as  $\text{AgBr}$ . Precipitate  $\text{AgBr}^*$  was transferred to filter paper in a uniform layer, carefully washed and lacquered. The obtained sample served for determination of the activity. In addition, corrections were introduced for errors in counting and for self absorption.

In experiments with other alkyl halides, the separation was carried out by the method of extraction of alkyl halide with cyclohexane or benzene after the addition to an alcohol solution of twice the amount of water. Special experiments indicated that sodium halide separates quantitatively from the alkyl halide as a result of triple extraction.

The alcohol-water fraction was titrated with a 0.1 N solution of  $\text{AgNO}_3$  according to Kolthof, in the case of  $\text{NaBr}$  or according to Fayance in the case of  $\text{NaI}$ . Precipitates of silver halides were used for measurements of activity as described above.

The cyclohexanol layer, containing alkyl halide, was sealed in flasks and heated to  $100^\circ$  for 4 hours and the result was saponification of the alkyl halide. Upon opening the flask cyclohexanol and alcohol were removed by evaporation. The sodium halide solution and  $\text{NaOH}$  were neutralized by means of acetic acid and after that the ions of halide



were precipitated by  $\text{AgNO}_3$  as described above. The activity of the precipitated  $\text{AgX}^*$  was determined by a measuring device.

In all series of experiments "witnesses" were prepared - precipitates of  $\text{AgX}^*$  obtained from the original active  $\text{NaX}^*$ . At the same time as the preparation of the "witness" the same quantity of  $\text{NaX}^*$  was used as the quantity which was removed for the determination of each point of the kinetic curve. The data obtained as a result of the sample measurement allowed us to calculate the depth of the exchange with reference to the time duration of the reaction.

For calculation of the constant of the velocity exchange it is necessary to know the mechanism of the reaction.

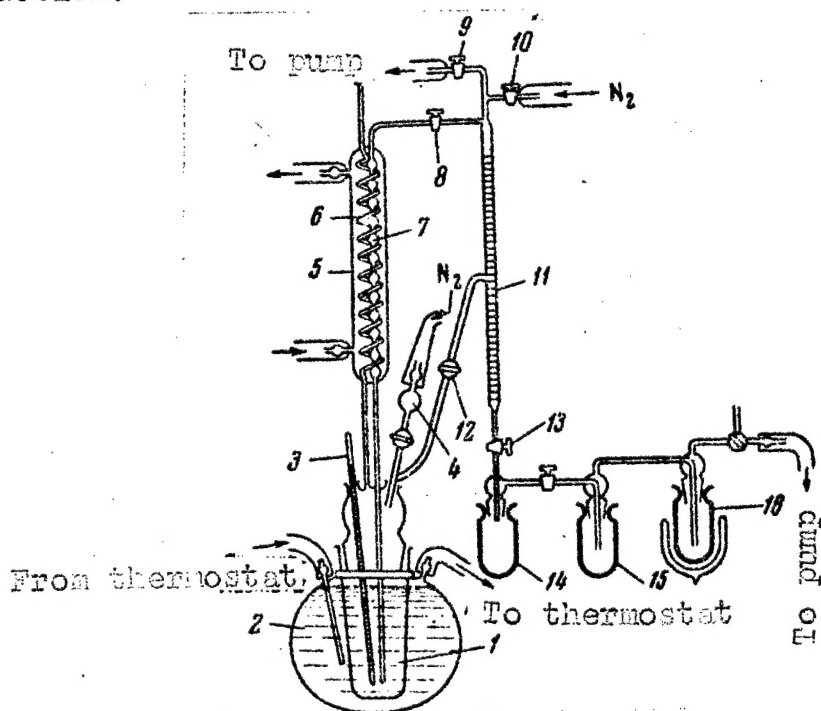


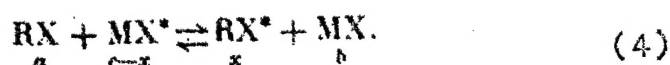
Fig 1. Scheme of installation for study of kinetics of isotope exchange ion reactions.

1 - reaction container; 2 - thermostat; 3 - thermometer; 4 - dropping funnel; 5 - condenser; 6 - spiral tube; 7 - ball type adapter; 8 - 9 - 10 - 12 - 13 - stopcocks; 11 - buret; 14 - 15 - 16 - traps.

# MECHANISM OF THE ISOTOPE EXCHANGE $RX + MX^*$

The isotope exchange may proceed according to one of the following schemes:

(a) Exchange according to molecular mechanism scheme:



Here R - organic radical, M - alkaline metal, X - halide atom, a and b concentrations of the exchanging substances, c - total quantity of the radioactive isotope, x - quantity of radioactive isotope, transferred into alkyl halide as a result of the reaction.

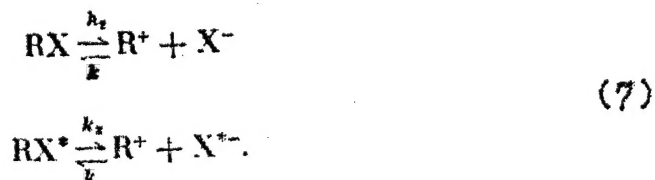
If the exchange proceeds according to the molecular mechanism, the change in the activity of the halide in time must be expressed by an equation:

$$\frac{dx}{dt} = k_1 a (c - x) - k_2 b x. \quad (5)$$

The velocity constant of the isotope exchange in this case should be calculated according to the formula

$$k_1 = - \frac{2.3}{(a+b)t} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (6)$$

(b) The exchange proceeding by way of alkyl halide dissociation on ions:





The growth of the halide activity in this case can be expressed by a differential equation

$$\frac{dx}{dt} = k[R^+][X^-] - k_2[RX^*]. \quad (8)$$

— If the activity coefficient of the ion  $X^-$  is equal to "f" then from the stipulation of the equilibrium of the alkyl halide dissociation it follows that

$$k[R^+] = k_2 \frac{[RX]}{[X^-]} = \frac{k_2 a}{fb}. \quad (9)$$

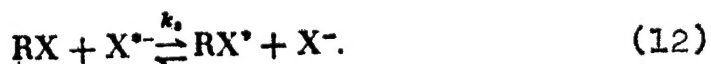
Substituting the value  $K[R^+]$  from the Equation (9) into Equation (8) and using the previous designation we have

$$\frac{dx}{dt} = \frac{k_2 a}{fb} f(c - x) - k_2 x. \quad (10)$$

The isotope exchange velocity in this case does not depend on the activity coefficient "f". Integration of Equation (10) results in the following equations for calculation of the isotope exchange velocity:

$$k_2 = - \frac{2,3b}{(a+b)t} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (11)$$

(c) Exchange according to molecular-ion mechanism proceeds according to the scheme



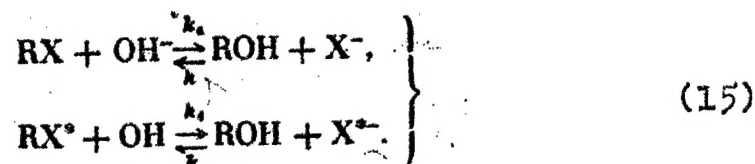
In this case the isotope exchange kinetics can be expressed by the equation:

$$\frac{dx}{dt} = k_3 fa(c - x) - k_3/bx, \quad (13)$$

Its integration results in a formula for calculating the constant

$$k_3 = - \frac{2,3}{(a+b)ft} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (14)$$

(d) Exchange by way of reversible reaction of seponification proceeds according to the scheme:



From the conditions of equilibrium it follows that

$$k[\text{ROH}] = \frac{k_a a [\text{OH}^-]}{fb}. \quad (16)$$

By utilizing Formula (16) it is possible to present an equation expressing the growth of the alkyl halide activity in the following manner:

$$\frac{dx}{dt} = \frac{k_a a [\text{OH}^-]}{fb} / (c-x) - k_a x [\text{OH}^-]. \quad (17)$$

In this case "f" is eliminated and for the velocity constant of the isotope exchange, the following formula results:

$$k_4 = - \frac{2,3b}{(a+b)[\text{OH}^-]t} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (18)$$

As is apparent from a comparison of Formulas (6), (11), (14), and (18), by means of kinetic experiments with various values of concentration of a and b re-

acting substances and various values of pH of the medium, it is possible to determine which one of the above-mentioned mechanisms actually takes place.

First of all, our investigation of the isotope exchange  $RX + NaX^*$  where  $R = CH_3$ ,  $C_2H_5$ , or  $C_3H_7$ , and  $X = Br$  or  $J$  demonstrated that saponification of alkyl halides under the conditions of our experiments proceeds with extreme slowness, and that the growth of concentration of ions  $X^-$  during the experiment may be neglected. This was substantiated by the titration results of ions  $Br^-$  and  $J^-$  at various intervals of time. As an example we present some of the obtained data in Table 2.

Table 2

Results of titration  $Br^-$  and  $J^-$  at various times during the conduct of the isotope reaction exchange

Substance	$t^\circ C$	$\%$	Results of titration during various moments of time
$CH_3CH_2CH_2Br$ . . . . .	75	12,03	12,02; 12,05; 12,04; 12,04
$CH_3CH_2CH_2J$ . . . . .	70	24,83	24,81; 24,83; 24,56; 24,86; 24,84
$CH_3CH_2CH_2$ . . . . .	60	8,1	8,03; 8,15; 8,11
$CH_3CH_2CH_2$ . . . . .	20	8,80	8,90; 8,77; 8,80; 8,80; 8,75

The data indicates small probability that the isotope exchange of the alkyl halides studied by us proceeds according to mechanism (2). However, a final conclusion with reference to non-correspondence of the mechanism (2) can only be made by means of investigation of the effect of the changing pH on the velocity of the isotope exchange.

Such experiments are described by Le-Roux and S. Sugden [16]. Certain data obtained by the authors relative to the isotope exchange velocity  $C_4H_9Br + LiBr^*$  is indica-

ted in Table 3.

Table 3

The constant of the isotope velocity of  
 $C_4H_9Br + LiBr^*$  at different pH

T°K	pH				Δ%
	1,3	7,0	11,0	12,7	
303	7,5	7,3	—	—	3
307,5	—	9,8	11,1	—	13
317,5	—	21,6	—	22,6	5

As is apparent from the data given in the table, the change in pH within wide limits corresponding to the change in values of  $[OH^-]$  by 11 orders does not practically lead to the change in the constant of the isotope exchange velocity. Therefore, the results of the experiment can not be presented according to Formula (18). This means that the isotope exchange is not related to the reaction of radical saponification.

Table 4

Kinetics of isotope exchange  $C_3H_7Br + NaBr^*$  at  $75^\circ C$ 

Concentration mole/l	min	Imp./min.		$\frac{x}{c}$	$k \cdot 10^4$		
		x	c		$k_1$ l/mole sec	$k_2$ sec <sup>-1</sup>	$k_3$ l/mole. sec
$a = 0,1$ $b = 0,0125$	30	29	316	0,0918	62	0,062	73
	180	118		0,373			
	240	163		0,516			
	300	182		0,576			
$a = 0,1$ $b = 0,1$	30	32	437	0,073	56*	5,6*	74*
	75	75		0,183			
	90	85		0,194			
	180	106		0,243			
	420	130		0,297			
$a = 0,6$ $b = 0,6$	5	5	102	0,049	34	20	73
	15	17		0,166			
	60	42		0,412			
	130	50		0,49			
$a = 1,0$ $b = 1,0$	15	27	201	0,134	27	27	71
	32	70		0,348			
	120	99		0,493			

\*Calculated according to experimental data obtained at  $75^\circ C$  and applying the value  $E = 18,000$  cal./mol [17].

In order to make a proper selection between the mechanisms (1), (2), and (3), we arranged a series of experiments related to the study of isotope exchange kinetics  $C_3H_7Br + NaBr^*$  in 90 percent ethyl alcohol at  $75^\circ C$ . In these experiments  $[C_3H_7Br] = a$  was changed from 0.1 to 1 mole/l and  $[NaBr] = b$  from 0.01 to 1 mole/l. The results of this experiment are shown in Table 4.

Utilizing the data presented in Table 4, we calcu-

lated values  $\lg\left[1 - \left(1 + \frac{b}{a}\right)\frac{x}{c}\right]$  and recorded their va-

lues for different times of the experiment in Fig 2. The experimental points are arranged along a straight line, originating from the origin of the coordinates, as it should be in the case of the isotope exchange reactions, independently from their mechanism. The values of constants  $k_1$ ,  $k_2$ ,  $k_3$  were calculated using the values of the straight line slope. The value  $-\frac{1}{t}\lg\left[1 - \left(1 + \frac{b}{a}\right)\frac{x}{c}\right]$

for  $k_1$  was multiplied by  $\frac{2.3}{a + b}$  and for calculation of  $k_2$

by  $\frac{2.3b}{a + b}$  in accordance with formulas (6) and (11), where-

as the mean values of individual weight determinations as given in Columns 6 and 7, Table 4 were considered.

From Table 4, it appears that the value  $k_1$  and  $k_2$  are not constant during the change in the concentration of the reacting substances. For that reason the molecular mechanism and the mechanism connected with dissociation of the alkyl halides on ions cannot be considered as suitable for explanation of the alkyl halide kinetics of isotope exchange with halides of sodium in the studied systems by us.

For calculation of  $k_3$  by Formula (14) it is necessary to know the value of "f". Inasmuch as there are no publications relative to measurements of active coefficient  $\text{H}\alpha\text{Br}$  in alcohol-water solutions, we roughly determined this value by measuring the electroconductivity of  $\text{H}\alpha\text{Br}$  solutions of various concentrations in  $\text{C}_2\text{H}_5\text{OH}$  containing 10 percent water [18]. The results of our measurements are given in Table 5.

Table 5

Determination of activity coefficient NaBr

c, mole/l	$\times 10^4$	$\frac{1000x}{c}$	$f = \frac{1}{\infty}$
1.0	149.9	15	0.41
0.5	93.1	18.6	0.50
0.25	54.9	22.0	0.60
0.125	31.2	24.9	0.68
0.0625	17.5	28.0	0.76
0.03125	9.6	30.7	0.83
0.01042	3.6	34.7	0.94
0.0052	1.9	36.7	1.0

The values of "f" were used for calculating  $k_2$  according to Formula (14), and in this case while calculating mean values of  $K_3$  the weights of separate experiments were considered.

As is apparent from examining Column 8, Table 4, the value of  $K_3$  is constant within  $\pm 3$  percent, regardless of the fact that the concentration was changed by a factor of 100.

The obtained results lead to the consideration that the isotope exchange in the  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{NaBr}^*$  mixture studied by us and also in other analogous systems proceeds according to a molecular-ion mechanism.

Evans and Sugden arrived at similar conclusions while studying isotope exchange in solutions of butylbromine and LiBr in acetone [19]. However, they failed to arrive at general conclusions from their own experimental results; in particular, they incorrectly considered that in alcohol solutions the isotope exchange proceeds according to a molecular mechanism. Meanwhile in their own experiments the velocity constant in alcohol solutions regularly increased by 11 percent with the decrease of concentration of from 0.023 to 0.00023 mole/l (calculated by our Formula 6). This value corresponds exactly to the growth of the activity coefficient of  $\text{I}^-$  ions at the noted increase of dilution, as is evident from the data given in Table 5.



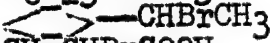
As for the intimate mechanism of the process, it is probable that during the reaction of the isotope exchange of this type the halide ion approaches the alkyl halide molecule from the side opposite to the location of a halide atom as shown in Fig 3.

According to Polyany [20] the reaction consists in transferring of the carbon atom C, connected with X, A, B, and D in a direction toward the ion X as indicated by the arrow in Fig 3. At the same time, atom C crosses the side of the tetrahedron ABD and the electron moves to atom X. As a result there occurs a reaction of isotope exchange and the end products are formed CX\*, ABD, and X<sup>-</sup>, shown at the right part of Fig 3. This scheme indicates that the energy of activation of the isotope exchange RX + X\* is connected with the necessity of overcoming the energy barrier during the transition of atom C between the substitutes A, B, and D. The bond stability in this case has a secondary role. If this scheme, connected with "turning inside out" of the tetrahedron is correct, then the reaction of the isotope exchange of the optically-active alkyl halides should be accompanied by their racemization. For verification of this conclusion, Hughes [21-23] and coworkers studied isotope exchange of certain optically-active halide derivatives.

In Table 6 constants of the velocity of the isotope exchange determined by Hughes are compared with the constants of racemization velocity.

Table 6

Comparison of velocity of isotope exchange with velocity of halide racemization

Substance	T°C	$k \cdot 10^5$ 1/mole sec.	
		racemization	isotope exchange
C <sub>6</sub> H <sub>13</sub> CHJCH <sub>3</sub>	30	2.88 ± 0.03	3.00 ± 0.25
 CHBrCH <sub>3</sub>	30.2	3.18 ± 0.05	3.49 ± 0.37
CH <sub>3</sub> CHBrCOOH	22	5.82 ± 0.06	5.72 ± 0.30

The table indicates that the velocity of racemization in all cases and within the limits of experimental error coincides with the velocity of the isotope exchange. This testifies that the isotope exchange  $RX + X^{*-}$  in the considered cases proceeds according to a molecular-ion mechanism and is accompanied with "turning inside out" of carbonic tetrahedron.

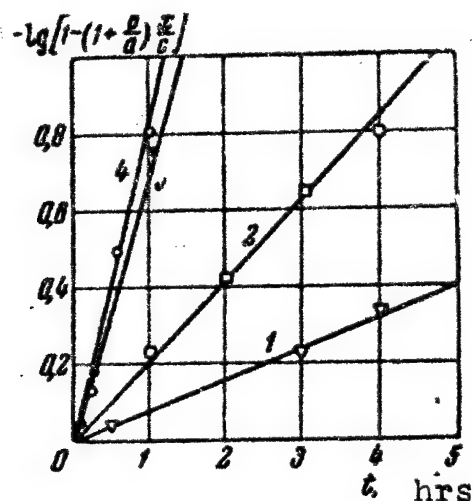


Fig 2. Straight line anamorphosis curves of the bromine isotope exchange between  $CH_3CH_2CH_2Br$  and  $NaBr^*$  at various reagent concentrations  
Line 1,  $a = 0.1$  mole/l;  $b = 0.01$  mole/l; line 2,  $a = b = 0.1$  mole/l; line 3,  $a = b = 0.6$  mole/l; line 4,  $b = b = 1.0$  mole/l;  $T = 75^\circ C$ .

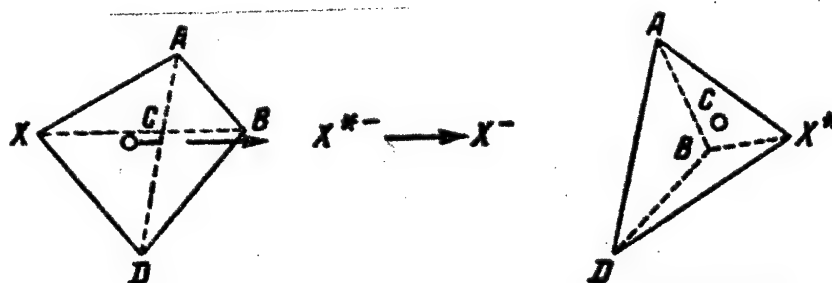


Fig 3. Reaction scheme of isotope exchange  
 $RX + X^{*-}$

## ISOTOPE EXCHANGE BETWEEN ALKYL BROMINE AND BROMINE IONS

As was pointed out in the introduction, the present work is dedicated to an investigation of the isotope exchange of simplest primary alkyl halides of normal structure and halide ions. Below are given the results of our experiments relative to exchange of  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{CH}_2\text{Br}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}^*$  with  $\text{Br}^-$ .

Experiments related to a study of kinetics of the isotope exchange of  $\text{CH}_3\text{Br}$  with  $\text{NaBr}^*$  in 90 percent  $\text{C}_2\text{H}_5\text{OH}$  were carried out at temperatures  $19.7^\circ$ ,  $37^\circ$ , and  $50.8^\circ\text{C}$ . The exchange was carried out in flasks submerged after sealing in an ultrathermostat. In all experiments the reagent concentration was equal to 0.1 mole/l. The results of the experiment are shown in Table 7. Straight line anamorphous lines (curves) of the rise of activity  $\text{CH}_3\text{Br}$  (Table 7) shown in Fig 4 allow us to judge the accuracy of the measurements carried out.

The velocity constants of the isotope exchange were calculated according to Formula (14). The most probable values of the constants were calculated according to the method of least squares considering the weight of separate determinations. Inasmuch as the relative errors while calculating a constant according to Formula (14) depend on the value of  $\bar{x}$ , we assigned to the calculated values of  $k$  a weight inversely proportional to relative errors. The weights of separate determinations are given in Column 6, Table 7. The most probable values  $k_2$  are given in Column 8 of the table, where in brackets are given also the mean quadratic errors in relative percentages.

Considering the inverse values of these errors as a measure for  $k$  determination at various temperatures, we calculated according to method of least squares the energy of activation of the isotope exchange reaction  $\text{CH}_3\text{Br} + \text{Br}^*$ . In this manner it was found that the most probable value of the energy of activation  $E = 17,500$  cal/mole.

Experiments in connection with the study of the isotope exchange velocity  $\text{C}_2\text{H}_5\text{Br} + \text{Br}^*$  in a solution of 90 percent ethanol were carried out at  $50^\circ\text{C}$ . The results of these experiments are shown in Table 8.

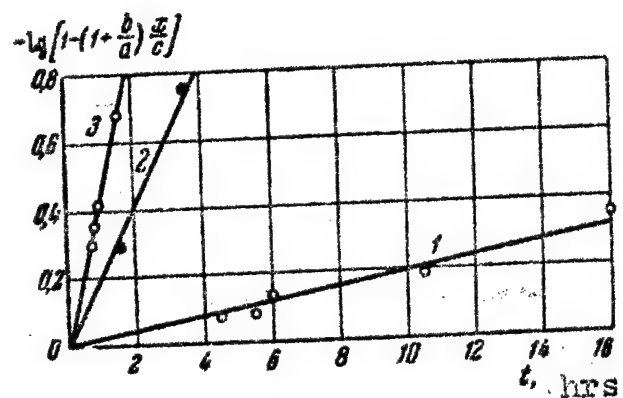


Fig 4. Straight line anamorphosis of curves of activity  $\text{CH}_3\text{Br}$  (Table 7)

Table 7

Kinetics of isotope exchange  $\text{CH}_3\text{Br} + \text{NaBr}^*$ ;  
 $a = b = 0.1 \text{ mole/l}$

$T^\circ\text{C}$	$t, \text{ hrs}$	Activity in imp/min		$\frac{x}{c}$	Weight determination	$k, \cdot 10^3$ l/mole. sec	$k, \cdot 10^3$ l/mole. sec
		$x$	$c$				
19.7	4.5	480	5870	0.08	0.35	7.8	9.4 (7.5%)
	6	840	5870	0.143	0.53	11.05	
	10.5	770	4290	0.18	0.68	8.25	
	16.2	350	1260	0.28	1.0	9.8	
37	1.4	127	493	0.257	0.86	94.5	97 (2.5%)
	3.5	213	493	0.43	0.85	99.5	
50.8	0.7	1380	5650	0.244	0.77	190	199 (3.6%)
	0.75	1560	5650	0.28	0.92	213	
	0.92	1640	2650	0.29	0.94	187	
	1.5	2230	5650	0.39	0.97	205	

Table 8

Kinetics of the isotope exchange  $C_2H_5Br + Br^{*-}$  at  $50^\circ C$   
 $a = b = 0.1$  mole/l;  $C = 470$  imp/min

t hrs.	Activity in imp/min	$\frac{x}{c}$	Weight determination	$k_3 \cdot 10^5$ l/mole sec	$k_3 \cdot 10^5$ l/mole sec
3.7	63	0.135	0.48	18.4	
6	82	0.175	0.65	15.8	17
8	110	0.235	0.78	17.5	(4%)

The treatment of the obtained data carried out as mentioned above indicated that the most probable value of the velocity constant of the isotope exchange in this case was  $K_3 = 17 \cdot 10^{-5}$  l/mole sec.

To this value  $k$  corresponds the approximate value of the energy of activation  $E \approx 18,000$  cal/mole.

The results of our experiments in connection with determination of the velocity constant of the isotope exchange  $CH_3CH_2CH_2Br + Br^{*-}$  in solution of 90 percent  $C_2H_5OH$  at six different temperatures are given in Table 9.

The energy of activation of this reaction  $E = 18,400$  cal/mole was determined by means of least squares from the obtained data.

Fig 5 gives the result of our experiments relative to determination of velocity of the isotope exchange  $CH_3Br$ ,  $C_2H_5Br$ , and  $C_3H_7Br$  with ions  $Br^{*-}$  and expressed in coordinates  $k$  and  $t$ .

As appears from the drawing, the maximum velocity of exchange is observed in the case of  $CH_3Br$  and minimum in the case of  $C_3H_7Br$ . The velocity constant of the isotope exchange for  $CH_3CH_2CH_2Br$ , determined only at  $50^\circ C$ , is located somewhat above the curve  $k = f(T)$  for  $CH_3CH_2CH_2Br$ . The probable curve of the relationship  $k$  from  $T$  for ethylbromine is shown by dotted lines. Therefore, our experiments lead to the conclusion that the velocity of the isotope exchange  $RBr + Br^{*-}$  decreases in accordance with the lengthening of the carbon chain of the radical  $R$ . This effect is particularly noticeable during the transition from  $CH_3$  to  $C_2H_5$ . Further lengthening of the carbon

chain decreases the velocity of the isotope exchange to a considerable extent. In order to establish to what extent the noted regularity has a general character, we executed similar investigations of the isotope exchange velocities with the simplest alkyl iodines with ions of iodine.

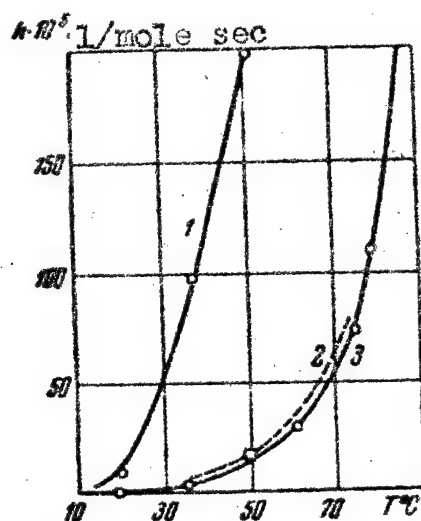


Fig 5. Temperature relationship between velocity of isotope exchange with bromine ions: curve 1 -  $\text{CH}_3\text{Br}$ , curve 2 -  $\text{CH}_3\text{CH}_2\text{Br}$  and curve 3 -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

Table 9

Relationship between velocity of isotope exchange  $\text{C}_3\text{H}_7\text{Br} + \text{Br}^*$  and temperature

$T^{\circ}\text{C}$	a. mole/l	b. mole/l	$k \cdot 10^3$ l/mole sec	quadratic error: %
19	0,23	0,12	0,46	13
35	0,1	0,1	3,6	8
61	0,1	0,1	30	9,5
73	(s. Table 4)	(s. Table 4)	73	2,7
79	0,1	0,1	111	6,4
100	0,1	0,1	478	3,3

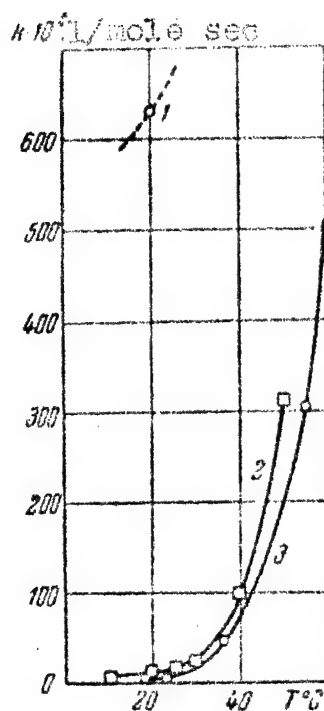


Fig 6. Temperature relationship between velocity of isotope exchange with ions of iodine: curve 1 -  $\text{CH}_3\text{J}$ , curve 2 -  $\text{CH}_3\text{CH}_2\text{J}$ , curve 3 -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{J}$

#### ISOTOPE EXCHANGE BETWEEN ALKYL IODINES AND IONS OF IODINE

The results of our investigation of the isotope exchange velocity  $\text{CH}_3\text{J} + \text{J}^{*-}$  in 90 percent ethanol at  $20^\circ\text{C}$  are given in Table 10.

The value of velocity of the exchange constant determined by us  $k = 630 \text{ l mole/sec}$  fully agrees with value  $k > 400$  quoted in works of Juliusburger, Topley, and Weiss



[24]. Methyl-iodide exchanges faster than any other alkyl halide studied in the present work.

Table 10

Kinetics of isotope exchange  $\text{CH}_3\text{I} + \text{I}^*$  at  $20^\circ\text{C}$   
 $a = b = 0.1 \text{ mole/l}$ ;  $c = 6350 \text{ imp/min}$

$t, \text{ min.}$	$x \frac{\text{imp}}{\text{min}}$	$\frac{x}{c}$	Weight determination	$k_3 \cdot 10^5$ 1/mole sec	$k_3 \cdot 10^5$ 1/mole sec
11	1330	0.21	0.72	588	
40	2280	0.45	0.75	687	
65	3090	0.486	0.4	654	630
120	3160	0.497	0.15	510	(3.6%)

The constant of the isotope exchange of ethyliodide with ions of iodine was not determined inasmuch as in published works [25, 26, 27] there are satisfactorily agreeing results of such determinations as is apparent from the data in Table 11.

All values of constants cited in the table were obtained from the quoted works by dividing by  $f$ , as the authors in all cases - while calculating constants - used Formula (6) and not (11).

As is apparent from a comparison of velocities of the isotope exchange at  $20^\circ\text{C}$ , ethyl iodine exchanges with iodine ions 40 times slower than does methyl iodine. The energy of the isotope exchange  $\text{C}_2\text{H}_5\text{I} + \text{I}^*$  is approximately equal to 19,000 cal/mole.

Table 11

Velocity constant of isotope exchange  $C_2H_5J + J^*$ 

T°C	[25]	[26]	[27]	$k_3 \cdot 10^5$
10	3.3	-	-	3
20	13.2	16	16	15
25	20	26	26	24
30	30.7	45	-	38
40	60	135	-	97
50	186	480	320	330

Table 12

Kinetics of isotope exchange  $CH_3CH_2CH_2J + J^*$   
 $a = b = 0.05$  l/mole;  $c = 7360$ 

T°C	t.hrs	$\frac{x_{imp}}{min}$	$\frac{x}{c}$	Weight determination	$k \cdot 10^5$ l/mole sec	$\bar{k}_3 \cdot 10^5$ l/mole sec
19						8.15 (6.6%)
22.5						10.0 (4.5%)
35.9	3.5	1440	0.19	0.68	47	46.3 (3%)
	6.68	2140	0.28	0.92	44	
	8.0	2570	0.34	1.0	43	
55	0.35	1030	0.135	0.5	311	304 (1.2%)
	0.45	1220	0.16	0.57	298	
	0.75	1830	0.24	0.8	304	
80.6	0.117	2130	0.28	0.92	2440	2460 (0.8%)
	0.167	2660	0.35	1.0	2480	

The results of our experiments [28] relating to the study of kinetics of the isotope exchange of  $CH_3CH_2CH_2I + I^*$  are cited in Table 12.

Using the data quoted in the table we calculated the

energy of this reaction to be  $E = 19,300$  cal/mole.

The effect of temperature on the velocity of the isotope exchange of  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ , and  $\text{C}_3\text{H}_7\text{I}$  with ions of iodine are given in Fig 6.

We observe that in the case of alkyl iodides, as in the case of alkyl bromides, the lengthening of the carbon chain radical slows the reaction of the isotope exchange  $\text{RI} + \text{I}^{*-}$ . At the same time a particularly strong effect was observed in the transition from  $\text{CH}_3\text{I}$  to  $\text{C}_2\text{H}_5\text{I}$ .

### DISCUSSION OF RESULTS

The facts obtained in the present work indicate that the velocity of the isotope exchange  $\text{RX} + \text{X}^{*-}$ , where X is an atom of halide, decreases with the lengthening of the carbon chain of the radical. This is apparent from Table 13, where the values of the reaction velocities of alkyl bromide at  $50^\circ\text{C}$  are compared with the velocities of alkyl iodides at  $20^\circ\text{C}$ .

As follows from the theory of an activated complex, the constant of the reaction velocity is expressed as follows:

$$k = \frac{e k T}{h} e^{-\Delta S^\ddagger / R} e^{-E / RT} \quad (19)$$

Table 13

Constants of isotope exchange velocities  $\text{RX} + \text{X}^{*-}$   
 $k \cdot 10^5$  l/mole sec

$T^\circ\text{C}$	Compounds	Radical		
		$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{C}_3\text{H}_7$
50	RBr .....	200	17	14
20	RI .....	630	13	10

Therefore the change in the value of  $k$  during the change in the radical  $R$  structure may depend on the value of the active energy  $E$  and the entropy of the activated complex  $\Delta S^\ddagger$ . The significance of these values calculated according to our experiments are given in Table 14.

Table 14

Values of  $E$  and  $\Delta S^\ddagger$  for some reactions of halide isotope exchange

Alcylhalide	$E_{\text{cal}}$ mole	$\Delta S^\ddagger$ cal mole grad
$\text{CH}_3\text{Br}$	17500	19.5
$\text{C}_2\text{H}_5\text{Br}$	18000	22.7
$\text{h-C}_2\text{H}_7\text{Br}$	18400	22.0
$\text{CH}_3\text{J}$	15400	19.5
$\text{C}_2\text{H}_5\text{J}$	19000	17.4
$\text{h-C}_3\text{H}_7\text{J}$	19300	13.3

From the information given in the table it appears that the changes in the equilibrium constant depend on the changes of the activated barrier and the energy of the activated complex.

At the present time we lack sufficient data for determining the connection between the changes in the radical  $R$  structure and the changes in  $\Delta S^\ddagger$  and  $E$ . Nevertheless, it is possible to state a theory that the value of  $E$  is connected basically with the height of the energy barrier which necessarily must be crossed during the transition of a  $C$  atom between the three substitutes and this conditions the inversion of the configuration during the isotope exchange of  $\text{RX}$  with ion  $\text{X}^-$ . In the case of  $\text{CH}_3\text{X}$  a  $C$  atom passes through the triangle side of the tetrahedron at the apex of which are located three atoms of hydrogen. In this case the height of the energy barrier is a minimum. In the case of  $\text{C}_2\text{H}_5$  at the apex of this side there are located two atoms of hydrogen and a radical  $\text{CH}_3$ . Apparently the exchange of one of the hydrogens with radical  $\text{CH}_3$  results in an increase of the energy barrier. Complication of the radical, for instance substitution of methyl with ethyl, results only in an insignificant rise of the barrier. It is possible to

theorize that the substitution by methyl radicals of not one but two atoms of hydrogen in a molecule  $\text{CH}_3\text{H}$  will result in an increase of the energy barrier to an even greater degree.

### CONCLUSIONS

1. The isotope exchange of saturated polyhalide derivatives of an aliphatic series with sodium halide in alcohol solutions operates according to a molecular-ion mechanism connected with inverse configuration.

2. The lengthening of the carbon chain in the radical R results in retardation of the isotope exchange between alkylbromides and alkyl iodides with ions of halides in alcohol solutions. The greatest effect is observed during passing from radical  $\text{CH}_3$  to radical  $\text{C}_2\text{H}_5$ .

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Entered 20 October 1953

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